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(54) Process for hydrogenation of oils.

(57) There is disclosed a process for hydrogenation of vegetable or animal oils, wherein the oil is hydrogenated, optionally in a solvent, with a hydrogen donor in the presence of a phase transfer catalyst, which reduces the iodine values of the starting materials from the values of 50 to 183 to the values of 10 to 150. According to said process, hydrogenation products having very good properties are obtained.

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PROCESS FOR HYDROGENATION OF OILS

Technical Field

The invention relates to the field of food technology and refers to a process for hydrogenating vegetable and animal oils or fats into products with unique melt profile by means of catalytic hydrogen transfer from an appropriate donor as well as to the products of said hydrogenation.

Technical Problem

There was a need to provide a process for preparing hydrogenated oils having special characteristics such as solid content index (SCI), iodine value (IV) and great stability at higher temperatures as well as to provide a simple and rapid one-step process for preparing said hydrogenated oils.

Prior Art

Textural characteristics of products which contain hydrogenated oils, such as margarines, ice-creams, cakes etc., particularly "mouthmelt", result from solid content index (SCI) of hydrogenated oils. There is a need for a novel and effective hydrogenation process in order to accomplish the preparation of fats with the desired melt properties and to provide the desired melt characteristics anticipated with SCI values 40 - 70, 45 - 65 and 10 - 30, in the temperature range from 10 °C to 30 °C. The basic hydrogenation process means the conversion of liquid oils into semi-solid substances and partially hydrogenated oils. Plastic fats are useful for preparing vegetable fats, margarine and special purpose fats. By means of hydrogenation there is also achieved increased stability and improvement of the basic colour.

Hydrogenation represents the double bond addition in fat in the presence of a metallic catalyst. The purpose of the hydrogenation is the saturation of double bonds of fatty acids in fats. The hydrogenation reaction is not simple since it is accompanied by the simultaneous double bond isomerization, which may be a positional or a geometrical one. The position of the fatty acid in glycerol (1, 2 and 3) as well as the degree of unsaturation determine the physical properties of the molecule, especially the melting point of the fat, and thence influences on SCI. The stepwise conversion of the most unsaturated fatty acid form proceeded to the saturated state, i.e. linolenic to linoleic, then to oleic, and finally to stearic. A very narrow melting range or a controlled level of trans acids cannot be achieved by a common hydrogenation.

In the literature there are described several methods for the hydrogenation of oils, especially vegetable oils, at temperatures from 190 °C to 230 °C and gauge pressures from 0 to 7.10^5 Pa (US patent 4,169,843 to Snyder et al. and US patent 3,459,777 to Selden et al.). According to the latter, the catalyst is added stepwise achieving the desired hydrogenation rate. The catalysts are a usual Ni catalyst or a sulfur-contaminated, i.e. deactivated Ni catalyst. General data can be also found in JAOCS vol. 60 (2), 1983, pp. 282-290, Beckmann "Hydrogenation Practice".

European Patent Application 0 246 366 A1 discloses a simplified one-step process with partly deactivated Ni catalyst at a temperature range from 160 to 250 °C and gauge pressure of hydrogen from 0 to 7.10^5 Pa.

The Inventive Solution

There is a one-step process presented in this case. All reactants are fed at once and react either in a batch reactor or in a continuous flow reactor where they flow over the catalyst prepared on an appropriate carrier. A hydrogen donor previously dissolved in a solvent or suspended in oil in the presence of a catalyst (preferably palladium) is used instead of molecular hydrogen. The process proceeds already at room temperature. Better results are achieved at 60 to 90 °C.

The hydrogenation is carried on at a temperature fro 20 to 90 °C, usually at room temperature and at atmospheric pressure. However, better results are achieved at higher temperatures.

The batch process is carried out in an organic solvent or in an aqueous emulsion. The continuous process, however, is carried out in an organic solvent.

Oils containing unsaturated fatty acids with at least 12 carbon atoms are hydrogenated. There are obtained products having specific compositions, which are the basis for producing margarine, creams, ice-creams etc., with improved edibility and appropriate melting properties as well as oxidation stability.

The oil acceptor (A) containing double bonds, the hydrogen donor (DHx) and the catalyst are in contact.

The hydrogen donor may be any organic compound having sufficiently low oxidation potential for carrying out the hydrogen transfer at relatively mild conditions.

The reaction takes place according to the following formula:

$$DHx + nA \xrightarrow{cat.} nAHx + D$$

The hydrogenation rate depends upon the nature of oil, the nature of hydrogen donor, the activity and the concentration of the catalyst as well as upon the velocity of the adsorption and desorption step of the unsaturated oil and the hydrogen donor on the catalyst. The compositions and properties of hydrogenated products can vary with regard to the position of the double bonds to be hydrogenated and are due to the influence of the isomerization reactions, which accompany each hydrogenation step. They also largely depends on hydrogenation conditions.

Vegetable oils or mixture of vegetable oils, which are suitable for hydrogenation, are e.g. soya oil, sunflower oil, safflower oil, maize oil, olive oil, bamboo oil, peanut oil, palm oil, rape oil, grape oil, coconut oil, pumpkin oil and castor oil.

As animal oil cod-liver-oil or a mixture of cod-liver oil with vegetable oils may be used.

There are used regenerable catalysts such as 1 - 20% palladium on active carbon (Pd/C), Pd/C/$FeCl_3$, Pd/C/Fe(III) hydroxide or oxide, 0.04 - 10% Pd/Al_2O_3, 5% Pt/C. 5% Pt/Al_2O_3, 5% rhodium on active carbon, Raney nickel, ruthenium black and platinum black.

There are used from 0.03 - 1.5% of the catalyst with regard to the starting mass of oils or fats.

The hydrogen donor must correspond to the catalyst, therefore formic acid and hypophosphorous acid as well as the salts thereof, such as triethylammonium formate, tri-n-butylammonium formate, sodium formate, potassium formate and ammonium formate as well as sodium hypophosphite are used.

The coordination of the interactions between the solvent, the donor and the hydrogen acceptor is very important when hydrogenation takes place in a solvent. If the bond between the solvent and the catalyst is stronger than the bond between the donor and the acceptor, the catalytic transfer reaction does not take place. Solvents such as ethanol propan-2-ol, formic acid, acetic acid, acetone and ethyl acetate may be selected. Some solvents can also act as the hydrogen donor.

The reaction may be directed into products, which may be totally or only partly hydrogenated oils. The reaction is especially suitable for obtaining partly hydrogenated oils. From soya oil, rape oil or some other vegetable oil, only within a few hours of hydrogenation, an oil containing less than 1 % linolenic acid is obtained.

Starting from cod-liver oils having high contents of poly-unsaturated ω3 acids (especially C18:3ω3, C20:5ω3 and C22:6ω3), there are obtained fats with lower iodine values and adequate melting properties.

In comparison with Prior Art processes, transfer reduction has real and potential advantages. Molecular hydrogen is easily ignited and presents considerable hazards, particularly in large plants. When using hydrogen donors, no gas containment is necessary. no pressure vessels are needed and a simple stirring of the solutions is usually all that is required. This process is very effeicient, energy-saving and there is also a great possibility of catalyst regeneration. The choice of the hydrogen donor can affect the reaction through its competitive adsorption onto the catalyst. The selectivity of the reduction process is considerably enhanced.

The continuous process is also very simple since neither mixing nor catalyst removal are necessary. The catalyst may also be regenerated in a column and can be used for almost an unlimited period of time. However, one disadvantage of the present process can be present, the solvent and the donor must be removed from the final product before its application.

In the batch process there is no need to use the organic solvent. The hydrogenation may take place in a water emulsion, excluding any problems regarding solvent or donor removals. After the completion of the reaction the aqueous and the oil phase separate and the water-soluble donor remains in the aqueous phase.

EXAMPLES

In the batch process, weight amounts of oil, catalyst and hydrogen donor, dissolved in an organic solvent or water, were agitated mechanically at about 900 rpm in a 150 ml flask which was immersed in a water bath at chosen temperature.

In the continuous process (Example 3) oil and hydrogen donor were dissolved in an organic solvent and

this solution was eluted through a column (30 x 1 cm) filled with celite (up to a height of 1 cm) and catalyst.

Example 1 (batch hydrogenation in organic solvent)

To oleic acid (1 ml), acetone (25 ml), formic acid (0.5 ml), triethylamine (2 ml) and 10% Pd/C (100 mg) were added. The mixture was mechanically stirred for 15 hours at room temperature and atmospheric pressure. After the removal of the solvent, mainly stearic acid was obtained. About 10% of oleic acid remained unreacted.

Example 2 (batch hydrogenation in organic solvent)

To sunflower oil (1 ml) having an iodine value (IV) of 139.2, acetone (25 ml), formic acid (0.5 ml), triethylamine (2 ml) and 10% Pd/C (100 mg) were added. The mixture was mechanically stirred for 15 hours at room temperature and atmospheric pressure. After the removal of the solvent a hydrogenated product with an iodine value of about 20 was obtained.

Iodine value was calculated from fatty acid composition.

In Table 1 the fatty acid composition of sunflower oil and of the hydrogenated product is given.

TABLE 1

Fatty acid	sunflower oil (IV = 139.2)	hydrogenated oil (IV = 20)
palmitic acid (C16:0)	8.3	9.7
stearic acid (C18:0)	2.9	85.1
oleic acid (C18:1)	23.5	
linoleic acid (C18:2)	65.2	5.2
linolenic acid (C18:3)	0.1	0.0

Example 3 (continuous hydrogenation in organic solvent)

A mixture of sunflower oil (2 ml) having an iodine value of 139.2, acetone (25 ml) and formic acid (2 ml) was eluted through a column filled with celite and with 100 mg of Pd/C. The flow rate was 0.5 ml/min. After the removal of the solvent a hydrogenated product having an iodine value of 122.4 and with a fatty acid composition as given in the Table 2 was obtained.

TABLE 2

Fatty acid	sunflower oil (IV = 139.2)	hydrogenated oil (IV = 122.4)
palmitic acid (C16:0)	8.3	10.0
stearic acid (C18:0)	2.9	3.0
oleic acid (C18:1)	23.5	38.5
linoleic acid (C18:2)	65.2	48.5
linolenic acid (C18:3)	0.1	0.0

Example 4 (batch hydrogenation in an aqueous emulsion)

To refined soya oil (15 ml) having an iodine value of 135.2 and a determined fatty acid composition, Pd/C (112.5 mg) was added. To this suspension sodium formate (18 g). previously dissolved in water (30 ml), was added. The emulsion was mechanically stirred for 33 hours at about 900 rpm, at a temperature of 60 °C and at atmospheric pressure. Samples were withdrawn periodically from the batch and analyzed for fatty acid compositions, melting points (MP), solid content index (SCI), trans contents (the content of positional and geometrical isomers of fatty acids - probably mainly in trans form) and the iodine value (IV) was calculated afterwards. The iodine value, the fatty acid composition and the trans content were determined by means of a gas chromatograph equipped with an ion trap detector.

IV (iodine value)	72	
MP (melting point)	38 °C	
SCI (solid content index)	10 °C	63.4
	15 °C	60.2
	20 °C	53.0
	25 °C	40.8
	30 °C	24.7
	35 °C	10.8

TABLE 3

Change in fatty acid composition of soya oil during hydrogenation and the content of trans acids

t(h)	C 18:3	C 18:2	C 18:1	C 18:0	C 16:0	% trans*
0	7.5	51.7	23.4	5.4	10.5	1.5
1	4.7	48.6	30.7	5.5	10.5	3.7
3	1.9	40.7	41.2	5.6	10.6	8.5
9	-	22.0	60.5	7.0	10.5	15.1
24	-	7.0	75.1	8.4	10.5	33.0
33	-	1.4	77.3	10.8	10.5	33.1

* Positional and geometrical isomers of fatty acids expressed as percent of total fatty acids.

Example 5 (batch hydrogenation in water emulsion)

The hydrogenation of rape oil having an iodine value of 132.2 containing 1.3% of erucic acid was carried out in the same manner as in Example 4, with the exception that the emulsion was heated for 16 hours at 80 °C. The iodine value, the melting point and the solid content index of the product were determined.

IV	95	
MP	26 °C	
SCI	10 °C	28.2
	15 °C	22.3
	20 °C	16.5
	25 °C	11.9
	30 °C	7.3
	35 °C	5.3

Example 6 (batch hydrogenation in water emulsion)

The hydrogenation of cod-liver oil having an iodine value of 162 was carried out in the same manner as in Example 4, with the exception that Pd/C (200 mg) was added and the emulsion was heated at 80 °C for 16 hours. The iodine value, the melting point and the solid content index of the product were determined.

IV	84	
MP	35 °C	
SCI	10 °C	45.5
	20 °C	35.2
	30 °C	10.7

Claims

1. A process for the hydrogenation of vegetable or animal oils or fats, characterized in that the oil is hydrogenated, optionally in a solvent, with a hydrogen donor in the presence of a phase transfer catalyst, which reduces the iodine values of the starting materials from the values of about 56 to 183 to the values of about 10 to 150.

2. A process according to claim 1, characterized in that as the hydrogen donor formic or hypophosphorous acid or their salts, such as triethylammonium, tri-n-butylammonium. sodium, potassium or ammonium formate and sodium hypophosphite are used.

3. A process according to claims 1 and 2, characterized in that vegetable oils or animal fats or mixtures thereof composed of fatty acids having at least 12 carbon atoms in a chain are used.

4. A process according to claims 1 to 3, characterized in that the vegetable oils are soya oil, sunflower oil, pumpkin oil, safflower oil, maize oil, olive oil, bamboo oil, peanut oil, palm oil, rape oil, grape oil, coconut oil and castor oil.

5. A process according to claims 1 to 4, characterized in that cod-liver oil or a mixture of cod-liver oil with vegetable oils are hydrogenated.

6. A process according to claims 1 to 5, characterized in that palladium on active carbon, $Pd/C/FeCl_3$, Pd/C/Fe(III) hydroxide or oxide, Pd/Al_2O_3, Pt/C, Pt/Al_2O_3, rhodium on active carbon, Raney nickel, ruthenium black or platinum black catalysts are used.

7. A process according to claims 1 to 6, characterized in that 0.03 to 1.5% of the catalyst with regard to the input mass of oils or fats is used.

8. A process according to claims 1 to 7, characterized in that the hydrogenation takes place at atmospheric pressure in a temperature range from 20 to 90 °C.

9. Hydrogenated oils and fats according to claims 1 to 8, characterized in that said product in case of partly hydrogenated oils contains under 1% of linolenic acid.

10. Hydrogenated oils and fats according to claims 1 to 9, characterized in that said content indexes thereof at the temperature of 10 °C amount to 40 - 70, at 20 °C 45 - 56 and at 30 °C to 10 - 30.

11. Hydrogenated oils and fats according to claims 1 to 10, characterized in that the solid content indexes thereof at the temperature of 10 °C amount to 20 - 50, at 20 °C to 10 - 40 and at 30 °C to 2 - 15.